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WORKING GROUP 5: MOLECULAR SPECTROSCOPY

A. Compendia. Bibliographies. Atlases

Research in molecular spectroscopy over much of the electromagnetic spectrum has continued intensively over the past three years. It has been stimulated not only by the imperatives of fundamental research programmes in many laboratories, but also by the impact of molecular lasers on the field, and the needs of atmospheric and environmental programmes. The literature is so prolific that it is impossible even to review briefly here all that is relevant to astrophysical needs. Thus most of this report has been compiled from the contributions from individual workers and Research Centres.

The bi-monthly Berkeley Newsletter(1) compiled from molecular spectroscopic publications in more than 30 journals continues to be a prime bibliographic tool for its more than 500 subscribers.

B. Molecular Data

1. ELECTRONIC BAND ANALYSES AND CONSTANTS OF DIATOMIC MOLECULES

Using laser spectroscopic methods Linton et al.(2) in a collaboration of workers from four laboratories, have continued their definitive studies of the CeO spectrum. The energies of 16 low lying states have been determined and quantum numbers assigned with certainty to 14 of them, and identification and analysis tables are provided for many bands.

Hirota and collaborators at the Institute of Molecular Science at Okazaki have an extensive programme on the microwave and infrared spectra of CH_3(3,4), HO_2(5), SiN(6), PO(7,8), HCCN(9) and FeO(10). Hefferlin(11) continues his theoretical and numerical studies on the systematic properties of constants of diatomic molecules.

2. TRANSITION PROBABILITIES, LIFETIMES, INTENSITIES

Dressler (Zurich) reports the following experimental and theoretical studies on f- values, lifetimes, and transition moments for band systems of NO, N_2 and H_2. Experimental and theoretical studies have been made on transitions between excited $^2\Pi$ states of NO by Gallusser and dressler(12). Similar work has been done for transitions between singlet states of N_2 by Stahel, Leoni and Dressler(13). An extensive study of lifetimes and transitions probabilities for a number of H_2 states and transitions between then are also reported(14-18).

Sharp (Munich)(19) has developed an efficient computational method for numerical evaluation of Morse Franck-Condon factors and r-centroids of molecular band systems.

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RESEARCH IN PROGRESS

A. From the Herzberg Institute of Astrophysics, National Research Council of Canada (Reported by A.R.W. McKellar)

Studies of the spectra of molecules of astronomical interest have continued to be the major activity in this laboratory. The diatomic molecules CH^+ (20), NH(21), BH^+(22), Geo(23), SiN(24), ClF(25) have been studied in the visible and ultraviolet regions. Infrared studies include the ions HeH^+(26), NeH^+(27), ArH^+ and KrH^+(28), as well as the neutral diatomics HN(29), SO(30), HD(31,32), SH(33), O_2(34), OH(35) and CH(36).

Significant advances have been made in the study of the triplet ground electronic state of the CH_2 radical, mostly involving the laser magnetic resonance technique. References to this work may be found in a paper(37) giving transition frequencies in the infrared and far infrared regions for astronomical purposes. Other triatomic molecules studied include NH_2(38-40), PH_2(41), NCO(42), CNO(43), HSO(44), HNO(45), FNO(46), and H_2S(47). The closely related ions NCO and NH_2^+ and their deuterated counterparts, were studied in the infrared(48-51). Interest continued in the spectrum of H_3^+ and its deuterated isotopes(52-54); molecules which are thought to play a key role in interstellar chemistry.

Following on from the study of the Rydberg spectra of neutral triatomic hydrogen, there has been considerable interest in the analogous spectrum of the ammonium (NH_4 and ND_4) radical(55-58). Studies of formaldehyde in the ultraviolet(59-62) and of thioformaldheyde, H_2CS, in the visible(63-70) have continued. In the infrared region, the CH_3 radical(71,72) and the H_3O^+ ion(73-75) have been studied, and extensive spectra of diacetylene have been analyzed(76). Prediction of the structure and spectra of SiH_3(77) and GeH_2(78) have been made and features due to the hydrogen dimer $(H_2)_2$, have been identified in the far infrared spectra of Jupiter and Saturn(79).

B. From the National Bureau of Standards (Reported by F.J. Lovas)

The Molecular Spectroscopy Division of the National Bureau of Standards carries out experimental studies on molecular spectroscopy in the microwave, infrared and visible regions of the spectrum and develops critical reviews on microwave spectra of interstellar molecules and tables of infrared absorption lines for calibration of diode laser measurements.

During the past three years several new reviews have been published or submitted. A review of the microwave spectra of ethanol (C_2H_5OH), and propionnitrile (C_2H_5CN) has appeared(80), and a review of SO_2(81) is in press. An update to a previously published table of rest frequencies for interstellar molecules is nearly finished(82). Compilations of infrared spectra include the species N_2O(83), OCS(84) and H_2O(85). A comprehensive review of vibrational energy levels of transient molecules was recently completed(86).

New laboratory studies in the microwave region have been published on BH_3NH_3(87), CH_2(88), CD_2(89) and H_2NSH(90). A matrix isolation study of CH_3CO and CH_2CHO was completed(91). Gas phase infrared spectra are reported for AlF and KF(92), benzene(93), ethane(94,95), SnO(96), OCS far infrared(97), CO(98) LiF(99) and CO_2(100). Analyses of electronic spectra of H_3(101) and ND_4(102) were also reported.

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C. From the Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory
(reported by W.H. Parkinson)

Since the last report we have used the 6.65 m vacuum scanning spectrometer/spectrograph(103) to make the following high resolution cross section measurements on molecules of atmospheric and/or astrophysical significance.

(a) Cross sections of the Schumann-Runge bands of O_2 at 300 K have been measured between 179.3 and 201.5 nm with an instrumental full width at half maximum (FWHM) of 0.0013 nm(104). Oscillator strengths of the (12,0) through (1,0) bands have been obtained by direct integration of the measured cross sections.

(b) Oscillator strengths for some rovibronic lines of the Schumann-Runge bands (13,0) through (16,0) or O_2 have been obtained between 176 and 179 nm, and the prospects for their use for Space Telescope observations of interstellar O_2 have been discussed(105).

(c) The absorption cross section of O_2 has been measured between 193.5 and 204.0 nm at 300 K and FWHM of 0.0013 nm. This spectral region contains discrete Schumann-Runge lines and underlying dissociation continua of the weak Herzberg I transition of O_2 and of the O_2 dimer. Analysis of the pressure dependence of the continuum cross section between the lines leads to Herzberg continuum cross sections smaller than previous laboratory values and in accord with recent *in situ* stratospheric measurements (106,107).

(d) Cross sections of O_3 at 195 K have been measured between 240 and 350 nm at a resolution of 0.003 nm, which is sufficient to resolve all of the fine structure present in the Hartley-Huggins bands(108).

(e) Cross sections of SO_2 at 213 K have been measured at a resolution of 0.002 nm from 172 to 240 nm(109). The results should be useful in elucidating the atmospheric compositions of Venus and Io.

(f) Cross sections of N_2O at 295-299 K have been measured between 170 and 222 nm with a resolution sufficient to yield cross sections that are independent of the instrumental function. Previously unresolved details of the banded structure which is superimposed on the continuous absorption between 174 and 190 nm are observed(110).

We have also compiled a photographic atlas of the Schumann-Runge absorption bands of O_2 between 175 and 205 nm(111).

In the microwave region of the spectrum, measurements on the submillimeter Zeeman spectra of OH(112) and HCO(113) have been completed. Fixed frequency lasers are used as radiation sources and the absorption spectra are scanned using the Zeeman effect. For comparison with astronomical submillimeter spectra, detailed theoretical calculations of the molecular Zeeman effect have been carried out by J.W. Brown and colleagues of the University of Southampton for OH. Similar calculation on HCO are almost complete.

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D. From the Centre for Research in Experimental Space Science, York University, Toronto (reported by R.W. Nicholls)

An experimental and theoretical research programme continues for the provision of transition probability and structure constant data for astrophysical and atmospheric molecules and applications.

An analysis of the rotational structure of the ClO violet bands has recently been completed by Morreau(114). Studies have continued on the line by line absorption coefficients of the absorption bands of ClO. The realistic spectrum synthesis facility developed in our laboratory has been applied to a wide range of atmospheric and astrophysical absorption spectra from the mm wave to the vacuum UV regions of the spectrum. Very recent studies include the synthesis of very high pressure oxygen(115) and long paths of CO_2(116). Such work has been applied to the extinction of sunlight in the atmosphere(117).

Studies have continued on the systematic properties of Franck-Condon factor arrays(118,119) and the relationship between simple harmonic oscillator Franck-Condon factors and those calculated for more realistic models(120). Studies have also been made on the geometry of principal and subsidiary Condon loci(121,122).

Analytical studies have been made of the wavelength dependence of Mie scattering coefficients(123). This work has led to an analytical form for the interstellar extinction function from the far IR to 100 nm(124,125).

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